

Title of the invention

Densifying hollow porous substrates by chemical vapor infiltration

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Background of the invention

The invention relates to densifying hollow porous substrates by chemical vapor infiltration (CVI), and more particularly doing so at pressure equilibrium, i.e. without
10 any pressure gradient between the faces of the substrates.

A particular field of application for the invention is making hollow parts out of a composite material comprising a porous substrate densified by a matrix, and in particular hollow parts made out of a thermostructural composite material.

The term "hollow porous substrate" is used herein to mean a substrate of hollow shape having a concave inside surface that is continuous, i.e. that does not have any holes, other than those due to the porous nature of the substrate. Examples of hollow shapes are spherical cap shapes, cylindrical or cylindro-conical shapes that are closed at one end, receptacle or bowl shapes, and cover shapes, not necessarily axially symmetrical. Examples of hollow parts obtained by densifying such substrates are receptacles for the
25 chemical and metallurgical industries, such as crucibles or crucible-support bowls, or protective bodies for spacecraft, such as nosecones that form heat shields.

The term "thermostructural composite material" is used herein to mean a composite material which presents both good
30 mechanical properties enabling it to constitute structural elements, and the ability to conserve these properties at high temperatures. Examples of thermostructural composite materials comprising a porous substrate of carbon fibers densified by a
35 carbon matrix, and ceramic matrix composite (CMC) materials

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comprising a refractory porous substrate, e.g. of carbon or ceramic fibers, densified by a ceramic matrix.

Densifying porous substrates by chemical vapor infiltration at pressure equilibrium is a well-known process.
5 The substrates to be densified are placed in an enclosure and a reactive gas is admitted into the enclosure where the temperature and pressure conditions are controlled in such a manner that the gas diffuses into the pores of the substrates and forms therein a solid deposit that constitutes the matrix
10 of the composite material either by causing a precursor gas to decompose or by causing a reaction to take place between a plurality of precursor gases contained in the gas. This applies, for example, to a carbon matrix where the gaseous precursor is generally an alkane, an alkyl, or an alkene, such as propane or methane or a mixture thereof. For a ceramic matrix made of silicon carbide, for example, the gaseous precursor is methyltrichlorosilane.

In general, the reactive gas is admitted into one end of the enclosure, while the effluent gas comprising the residue of the admitted gas and any reaction products is extracted from the other end. Admission advantageously takes place through a preheater zone serving to bring the admitted gas up to a temperature close to the temperature of the substrates for densifying.

25 A plurality of substrates can be densified simultaneously in a single enclosure, with the substrates being placed in such a manner as to ensure that all of them are exposed to the flow of reactive gas admitted into the enclosure. US patent No. 5 904 956 shows identical substrates disposed in a
30 particular manner in annular stacks for this purpose. The gas is admitted and directed towards the inside (or the outside) of the stacks and it flows through the substrates and the gaps between them so as to be taken up from the outside (or the inside) of the stacks.

35 When the substrates to be densified are hollow as defined above, having relatively deep concave portions, and in

particular when they are of quite large dimensions, defects have been observed by the inventors after densification by chemical vapor infiltration. These defects consist in variations in the microstructure of the material of the matrix 5 between different portions of the densified parts, and in the formation of soot or undesirable projections on the substrates.

Since these defects can be attributed to excessive maturation of the admitted gas, i.e. the admitted gas spends 10 too long in transit inside the enclosure and therefore ages, thereby spoiling its properties, attempts have been made to remedy that problem by increasing the gas flow rate by increasing the rate at which effluent gas is pumped out from the enclosure. However that has not made it possible to eliminate the defects completely, while it has considerably increased cost by increasing consumption of reactive gas.

Objects and summary of the invention

An object of the invention is to provide a method which does not present such drawbacks, i.e. a method that enables hollow-shaped substrates, even when of large dimensions, to be densified in a manner that is relatively uniform and free from defects.

This object is achieved by a method in which, in 25 accordance with the invention, part of the reactive gas flow admitted into the enclosure is guided by tooling to the inside of the volume defined by the concave inside face of the or each hollow-shaped substrate so that said concave inside face is swept in full by a fraction of the total admitted reactive 30 gas flow.

Advantageously, the reactive gas flow admitted into the enclosure is distributed towards each face of the or each substrate disposed inside the enclosure. Preferably, the fraction of the total reactive gas flow traveling over a face 35 of the or each substrate disposed inside the enclosure is not less than 5%, or better still 10%.

The inventors have observed that by guiding a fraction of the gas flow within the enclosure to the insides of the substrates, uniform densification is obtained without unwanted projections or soot being formed, even in the zones situated 5 most deeply inside the hollow shapes. This can be explained by the fact that guiding the flow forces the gas to flow along the internal concave faces of the substrates in full, without forming any pockets of stagnation or any turbulent zones in which excessive maturation of the gas might occur.

10 A portion of the gas flow can be guided by a wall portion that penetrates part of the way into the volume defined by the concave inside face of the or each substrate, e.g. a cylindrical wall portion which extends to the vicinity of the end wall of the or each substrate.

15 20 25 Advantageously, a plurality of hollow-shaped substrates can be densified simultaneously in the enclosure by being placed in alignment in the general direction along which the gas flows through the enclosure. The gas flow admitted into the enclosure is then distributed appropriately for feeding each of the faces of the substrates by corresponding fractions of the flow.

Another object of the invention is to provide an installation for densification by chemical vapor infiltration and enabling the above-defined method to be implemented, the 25 installation being adapted to densifying hollow-shaped substrates.

This object is achieved by an installation of the type comprising an enclosure having a side wall and first and second end walls opposite each other, means for admitting a 30 reactive gas opening out into the enclosure through the first end wall, means for evacuating effluent gas opening out into the enclosure through the second end wall, and at least one tray for supporting a substrate to be densified, which installation further comprises means for distributing and 35 guiding the gas flow so as to bring a fraction of the admitted gas flow to the location of each substrate within the

enclosure and so as to guide a portion of the gas flow brought to said location to the inside of a volume defined by a concave inside face of a substrate disposed at said location.

The flow guide means can comprise a cylindrical wall 5 portion or body presenting a plurality of through passages, the wall portion or body being placed in such a manner as to penetrate at least part of the way into said volume of the substrate.

The means for distributing the flow can comprise one or 10 more trays which extend transversely inside the enclosure and which define flow-distributing passages formed by openings made through the trays and spaces left between the trays and a side wall of the enclosure.

Brief description of the drawings

The invention will be better understood on reading the following description made below by way of non-limiting indication and with reference to the accompanying drawings, in which:

20 · Figure 1 is a highly diagrammatic fragmentary elevation and section view of a first chemical vapor infiltration installation constituting a first embodiment of the invention;

· Figure 2 is a half view in section on plane II-II of Figure 1 and as seen from above;

25 · Figure 3 is a highly diagrammatic fragmentary view in elevation and in section of a chemical vapor infiltration installation constituting a second embodiment of the invention;

· Figure 4 is a half view in section on plane IV-IV of Figure 3 and as seen from above;

30 · Figure 5 is a highly diagrammatic fragmentary view in elevation and in section on planes V-V of Figure 6 showing a chemical vapor infiltration installation constituting a third embodiment of the invention;

35 · Figure 6 is a section view on plane VI-VI of Figure 5 and as seen from above;

• Figure 7 is a highly diagrammatic fragmentary view in elevation and in section of a chemical vapor infiltration installation constituting a fourth embodiment of the invention;

5 • Figure 8 is a fragmentary section view showing a variant embodiment of tooling for guiding the reactive gas flow towards the concave inside face of a substrate;

10 • Figure 9 is a photograph showing the general appearance of the surface of a concave face of a substrate densified using a method in accordance with the invention;

15 • Figure 10 is a photograph obtained with an optical microscope showing a fraction of the surface of the concave face of the densified substrate shown in Figure 9;

20 • Figure 11 is a highly diagrammatic view of a chemical vapor infiltration installation of the prior art; and

25 • Figures 12 and 13 are photographs obtained with an optical microscope showing the surface state of samples after being densified using the installation of Figure 11.

Detailed description of embodiments of the invention

Figures 1 and 2 are diagrams showing an enclosure 10 constituting a reaction chamber for a chemical vapor infiltration installation.

30 In the example shown, the enclosure 10 is generally in the form of a vertical axis cylinder. A reactive gas is introduced into the enclosure via a pipe 12 which opens out for example through the center of a bottom wall 10a of the enclosure 10. Effluent gas is extracted from the enclosure via a pipe 14 which opens out through the center of the top wall 10b forming a cover that is remote from the bottom wall 10a. The pipe 14 is connected to pumping apparatus (not shown).

35 In the bottom portion of the enclosure, the gas passes through a preheater zone 16 constituted, for example, by horizontal perforated plates 18 which are placed one above

another. The plates 18 are supported on the bottom 10a of the enclosure by means of legs and spacers.

The preheater zone is separated from the reaction chamber proper by a horizontal diffuser plate 20 which occupies 5 substantially the entire cross-section of the enclosure 10. The diffuser plate 20 is perforated and stands on the bottom 10a of the enclosure via legs.

The above elements of the preheater zone are made of refractory material, e.g. graphite.

10 The inside of the enclosure is heated by a graphite susceptor which is coupled electromagnetically with an inductor (not shown) situated outside the enclosure. The susceptor forms the side wall 10c of the enclosure 10. The bottom wall 10a and the cover 10b are likewise made of graphite.

An installation as briefly outlined above is of well-known type.

In the example shown in Figure 1, a plurality of hollow-shaped substrates are disposed inside the enclosure 10 so as to be densified simultaneously, and specifically three such substrates S₁, S₂, and S₃ are disposed therein. The substrates shown are bowl shaped. By way of example they can be preforms for C/C composite material bowls that are to receive crucibles containing liquid silicon in an installation 25 for drawing silicon single crystals using the Czochralski or "CZ" process. Such bowls can have a diameter that is as great as or even greater than 850 millimeters (mm). The substrate or bowl preform is made of carbon fibers, e.g. by winding a filament or by draping fiber plies. Naturally, the invention 30 is not limited to densifying such substrates and it applies to densifying any substrate of hollow shape, such as those defined in the introduction to the present description.

The substrates are placed one above another, in alignment on the generally vertical direction in which the gas flows 35 through the enclosure, and the concave hollow faces of the substrates face downwards.

Each substrate S_1 , S_2 , S_3 stands on a respective support tray 22₁, 22₂, 22₃ with blocks 24 being interposed between the edges of the substrates and the top faces of the trays. The support tray 22₁ stands on the diffuser plate 20 via spacers 5 26₁, while the trays 22₂ and 22₃ stand on the trays 22₁ and 22₂ via spacers 26₂, and 26₃.

The blocks 24 leave gaps between one another so as to allow the gas to flow. They can be generally be in the form of circular arcs and their faces can engage in an annular groove formed in the top face of the support plate. Each block 24 can present an annular outer rim 24a on which the rim of the substrate comes to bear via its outside edge. The blocks 24 then act as shapers by preventing the substrates from deforming by expanding. The blocks 24 could also have respective inside rims.

The support trays, the blocks, and the spacers supporting the trays are all made of refractory material, e.g. a refractory metal or graphite.

The support trays 22₁, 22₂, and 22₃ also have the function of distributing the flow of the gas admitted into the enclosure and leaving the preheater zone. For this purpose, the trays are made of gasproof material, and present respective central orifices 28₁, 28₂, 28₃ while also leaving respective annular gaps 30₁, 30₂, 30₃ at their peripheries 25 relative to the side wall 10c of the enclosure.

The orifices 28₁, 28₂, 28₃ and the passages defined by the annular gaps 30₁, 30₂, 30₃ distribute the gas flow so that a fraction of fresh gas admitted into the enclosure reaches each location for a substrate in the enclosure and passes over 30 each face of a substrate disposed at said location. This fraction is at least 5% and preferably at least 10% by volume.

In the example shown, each of the inside and outside faces of the substrates S_1 , S_2 , and S_3 consequently receives preferably at least 10% and better still about one-sixth of 35 the flow of fresh gas admitted into the enclosure. The passage 30₁ receives the complement of the total admitted gas

flow relative to that which is received by the inside face of the substrate S₁ via the orifice 28₁. The passage 30₂ receives the portion of the admitted gas flow that has passed through the passage 30₁, and that is complementary relative to 5 the portion which is received by the outside face of the substrate S₁ and the portion which is received by the inside face of the substrate S₂ via the orifice 28₂. The passage 30₃ receives the portion of the admitted gas flow that has passed through the passage 30₂, and that is complementary relative to 10 the fraction which is received by the outside face of the substrate S₂ and which is received by the inside face of the substrate S₃ via the orifice 28₃. This remaining fraction of the admitted gas flow passing through the passage 30₃ feeds the outside face of the substrate S₃.

Each fraction of the gas flow passing through an orifice 28₁, 28₂, or 28₃ is guided towards the inside face of the end wall of the corresponding substrate by means of a respective guide wall 32₁, 32₂, or 32₃ provided at each location for a substrate inside the enclosure, and constituting gas flow guide tooling for the associated substrate.

Each guide wall is in the form of a cylinder or a length of pipe connected to a respective one of the orifices 28₁, 28₂, 28₃ and it projects above the corresponding support tray inside the volume defined by the substrate. Each guide wall 25 thus brings a fraction of the flow directly into the vicinity of the end wall region of the corresponding substrate. Each guide wall comes to an end at a distance from the inside surface of the corresponding substrate such that an annular gap is left relative thereto which provides a flow section 30 that is at least as great as the flow section provided by the orifice formed through the support tray.

The guide walls are made of a preferably gasproof refractory material, e.g. a refractory metal or graphite, or else a pyrolytic graphite sheet material such as provided 35 under name "SIGRAFLEX ®" by the German company SIGRI GmbH.

Because of the guide walls 321, 322, 323, a fraction of the admitted gas flow is forced to sweep over the inside faces of the substrates S₁, S₂, S₃ in full and to flow along said inside faces without leaving any dead volume and without creating any turbulence. It can thus be guaranteed that the transit time of the gas remains at all points below a limit value beyond which the maturation of the gas could become excessive and lead to unwanted deposits forming. As a general rule, the total transit time for the gas through the enclosure, i.e. the time that elapses between the gas being admitted and being removed must be limited. When the matrix is made of carbon, the transit time is generally controlled to remain below 2 seconds (s) and typically lies in the range 1 s to 1.5 s, for example.

The residual portions of the gas flow fractions that have flowed over the inside faces of the substrates are evacuated after passing through the gaps between the blocks 24. All of the effluent gas is collected together in the top portion of the enclosure and is evacuated via the pipe 14.

The chemical vapor infiltration process is of the pressure equilibrium type, i.e. there is no pressure gradient between the inside and outside faces of the substrates.

Although the above description relates to densifying three substrates simultaneously, the number of substrates present in the enclosure could naturally be other than three, for example it could be one, while still maintaining the possibility of organizing the gas flow so that a significant fraction thereof feeds each face of the substrate.

It is also possible to define a plurality of sets of substrates that are placed side by side inside an enclosure, each set comprising one or more substrates in alignment in the general flow direction of the gas. A plurality of admission orifices for the gas into the enclosure, and a plurality of orifices for removing effluent gas from the enclosure, together with a plurality of preheater zones can then be

provided, each in register with a corresponding set of substrates and support trays.

In addition, it is possible within a single enclosure to densify other hollow-shaped substrates that are different or
5 different in size from one another, possibly adapting the shapes and dimensions of the means for guiding the flow towards the insides of the substrates. It is also possible for the enclosure to contain other substrates that are not hollow in shape, or that are not so hollow as to require
10 special flow guidance means.

Figures 3 and 4 show a variant embodiment of the invention. The installation of Figures 3 and 4 differs from that of Figures 1 and 2 in that the support trays 122₁, 122₂, 122₃ do not stand on spacers, but instead stand on shelf-supports or pegs 126₁, 126₂, 126₃ engaged in the side wall 10c of the enclosure, so that the trays are supported like shelves.

The support trays can then occupy substantially the entire cross-section of the enclosure 10.

As in the embodiment of Figures 1 and 2, each support tray has a central orifice 128₁, 128₂, 128₃ having tooling for guiding the flow of reactive gas connected thereto in the form of respective cylindrical walls 132₁, 132₂, and 132₃.

Slots 130₁, 103₂, 130₃ are formed through the trays all
25 around annular zones thereof, outside the edges of the substrates S₁, S₂, S₃ so as to leave direct passages for fractions of the gas flow admitted into the enclosure, enabling the gas to flow through the planes occupied by the trays in a manner that is equivalent to the gaps 30₁, 30₂, 30₃
30 shown in Figures 1 and 2.

Figures 5 and 6 show another variant embodiment of the invention. The installation of Figures 5 and 6 differs from that of Figures 3 and 4 in that the support rays 222₁, 222₂, 222₃ which are supported by shelf-supports 226₁, 226₂, 226₃
35 carry respective pluralities of substrates, and specifically

three substrates such as the substrates S₃, S'₃, and S"₃ for the tray 222₃.

Each tray, e.g. the tray 222₃ has a plurality of orifices 228₃, 228'₃, and 228"₃ for directing a fraction of the gas flow towards each inside concave face of the substrates supported by the tray. Guide tooling formed by respective cylindrical guide walls 232₃, 232'₃, 232"₃ are connected to the respective orifices and project into the insides of the volumes defined by the corresponding substrates so as to guide said flow fractions to the vicinities of the end walls of the substrates. Slots 230₃ are formed in the tray 222₃ around the locations for the substrates S₃, S'₃, S"₃ so as to allow a fraction of the gas flow admitted into the enclosure to pass directly through the plane of the tray 222₃ around each of the substrates.

The trays 222₁ and 222₂ are made in the same manner as the tray 222₃, with orifices 228₁, 228'₁, 228₂, 228'₂ having guide walls 232₁, 232'₁ and 232₂, 232'₂ connected thereto and having slots 230₁ and 230₂.

The dimensions of the orifices and of the slots formed in the support trays are selected so as to ensure that the flow of fresh gas admitted into the enclosure 10 has the desired distribution as it flows towards the faces of the substrates.

A plurality of gas effluent evacuating pipes 214, 214', and 214" are preferably provided and united outside the enclosure, these pipes opening out into the enclosure in register with the tops of the substrates located on the top tray so as to ensure that the gas flow travels fully over the outside faces of these substrates.

In the embodiments described above, the substrates are placed inside the infiltration enclosure with their concave inside faces facing downwards, i.e. directed against the general flow direction of the reactive gas flow inside the enclosure.

The substrates could be disposed the other way up, as shown in Figure 7.

The embodiment of Figure 7 differs from that of Figure 1 in particular in that the substrates S_1 and S_2 are placed inside the enclosure 10 with their concave inside faces directed upwards.

5 Each substrate S_1 , S_2 has the outside face of its end wall standing on a plurality (at least three) blocks or studs 324₁, 324₂. The studs 324₁ are supported by a tray 316 that performs preheating and diffusion functions on the gas admitted into the enclosure by the pipe 12 which opens out 10 into the bottom of the enclosure, the gas inlet orifice being surmounted by a flow-distributing cap 318.

The studs 324₂ are fixed on a respective support tray 322₁ which stands on the diffusing tray 316 via spacers 326₂.

20 The support tray 322₁ presents a large central opening 328₁ while also leaving an annular gap 330₁ at its periphery relative to the side wall 10c of the enclosure.

In addition, the tray 322₁ overlying the substrate S_1 leaves an annular gap 331₁ relative to the top edge of the substrate.

25 A top tray 322₂ supported by spacers 326₂ is placed above the substrate S_2 in the same manner as the tray 322₁ is placed relative to the substrate S_1 . The tray 322₂ presents a large central opening 328₂ and leaves an annular gap 330₂ relative to the side wall of the enclosure, and an annular gap 331₂ relative to the top edge of the substrate S_2 .

The reactive gas flow admitted into the enclosure is distributed through the gaps 330₁, 330₂, and 331₂ so that a fraction of this flow is fed onto each of the faces of the substrates.

30 The flow fraction passing through the gaps 331₁ and 331₂ is guided towards the concave inside faces of the substrates S_1 and S_2 by means of tooling formed by respective guide walls 332₁ and 332₂. The guide walls are, for example, in the form of cylinders or segments of pipe, and they are supported by 35 the trays 322₁, 322₂ with their top portions being connected to the edges of the openings 328₁, 328₂. Each guide wall

penetrates a certain distance into the inside portion of the corresponding substrate so as to bring the flow admitted to the periphery down towards the bottom end wall of the substrate before flowing upwards through the pipe defined by
5 the guide wall (see arrows in Figure 7).

The residual gas flowing through the opening 328₂ of the top tray is evacuated by the pipe 24 which opens out in the cover 10b of the enclosure.

10 The guide walls 332₁, 332₂ thus force a fraction of the admitted reactive gas flow to sweep over the inside faces of the substrates S₁, S₂ and to flow along them without leaving any dead volume or without creating any turbulence.

15 Although the embodiment shown in Figure 7 shows only two substrate locations, the number of locations could naturally be greater than two, for example by placing more than two substrates one above another or by juxtaposing a plurality of sets of substrates themselves disposed one above another as shown in Figure 5.

20 In the above description, the tooling for guiding the flow of reactive gas is in the form of walls. Other forms of tooling could be adopted, as shown in Figure 8.

25 This figure shows only one substrate S₁ supported on a tray 422₁ by means of studs or blocks 424₁. The substrate S₁ is placed with its concave inside face directed downwards and it rests via its edge on the blocks 424₁. A stream of gas flows into an annular space 430₁ around the substrate S₁ and through the tray 422₁ so as to feed the inside face of the substrate S₁.

30 In its portion situated facing the inside face of the substrate S₁, the tray 422₁ presents a plurality of passages or perforations 423₁ and supports guide tooling 432₁.

35 The tooling 432₁ is in the form of a block, e.g. of graphite, of a shape that is similar and complementary to the shape of the inside volume of the substrate S₁ but it is smaller in size so as to leave a gap between the outside face of the block and the inside face of the substrate. The block

is pierced by a multitude of passages 433₁ which bring the gas that passes through the tray 422₁ to the vicinity of the inside face of the substrate, so that this inside face has the gas flow traveling thereover without leaving any dead volumes.

5 Although the description above relates to embodiments in which the general flow direction of the gas through the enclosure is upwards, the opposite disposition could be adopted with the general flow direction of the gas being downwards, in which case the preheater zone should be located
10 in the top portion of the enclosure.

Furthermore, the method of the invention can naturally be implemented on substrates of different dimensions received simultaneously within the enclosure.

15 Example

Substrates constituted by bowl preforms were densified using an installation of the kind shown in Figure 7. The substrates were built up from two-dimensional carbon fiber plies draped onto a shaper and consolidated by being impregnated with a resin followed by polymerization and carbonization of the resin.

The substrates were densified with a matrix of pyrolytic carbon by admitting a gas into the enclosure comprising natural gas or methane as the gaseous precursor for pyrolytic carbon.

The temperature and the pressure inside the enclosure were maintained substantially constant throughout the densification process, at values equal to about 1000°C and 1.5 kilopascals (kPa).

Once densification had been completed, no projections or soot formations were observed. The inside faces of the resulting C/C composite material bowls were of good appearance, as shown in Figures 9 and 10 where Figure 10 is an image obtained using an optical microscope, with $\times 440$ magnification, showing a fraction of the surface of the end wall of a bowl after densification.

By way of comparison, the same densification process was performed on similar preforms, but omitting the flow-guiding walls 332₁ and 332₂ and the central openings 328₁ and 328₂ in the trays 322₁ and 322₂, as shown in Figure 11. The substrates S'1 and S'2 were supported by the preheater plate 316 and by a solid tray 332'1 via blocks 321'1, 324'2 analogous to the blocks 324₁, 324₂ of Figure 7. Samples E₁, E₂ made of the same material as the substrates were placed respectively on the end wall of the substrate S'2 and beside it on the tray 322₁. Figures 12 and 13 are images obtained using an optical microscope with $\times 440$ magnification, in polarized light showing the surfaces of the samples E₁ and E₂ after densification. The presence of numerous projections and soot can clearly be seen on the surface of the sample E₁, in spite of the improvement provided by the presence of the trays compared with the situation in which substrates are placed without taking any precautions whatsoever on the substrates. Although the trays did not have any central openings and did not support any tooling for guiding the gas flow, they nevertheless helped to distribute gas flow via the gaps 330'1, 330'2, and 331'2.

In comparison, Figures 10 and 13 do not show any projections or soot of the kind visible in Figure 12, confirming that the method of the invention makes it possible to obtain the same quality on the inside surfaces of the end walls of hollow portions of a substrate as can be obtained on substrates that do not present such hollow portions.